

## METHODS FOR FABRICATING METAL NANOWIRES

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### CROSS-REFERENCE TO RELATED APPLICATION

This application is related to provisional U.S. Patent Application Serial No. 60/306,715 and Provisional U.S. Patent Application Serial No. 60/317,862, which applications are fully incorporated herein by reference.

### FIELD OF THE INVENTION

The invention relates to metal nanowires and, more particularly, to methods which facilitate the fabrication of long, free standing metal nanowires.

### BACKGROUND

Metal nanowires have great potential for immediate use in small electronic circuits, sensitive chemical sensors or any application requiring metal filaments, and will likely be required as interconnects in the nanometer-scale electronics of the future, especially those future electronics which are not based on existing silicon technology. However, there are few methods for preparing nanowires that have such technological utility. More particularly, few methods are capable of producing

nanowires that are long (i.e., greater than ten microns in length), uniform in diameter, free standing, and metallic. Two of the most successful approaches have been *template synthesis* and *step-edge decoration*.

The *template synthesis* method, which is described in publications by the research groups of M. Moskovits<sup>16-18</sup>, C.R. Martin<sup>8-15</sup>, and P.C. Searson<sup>21-27</sup>, appears to permit the growth of metal nanowires over a wide range of diameters (from nanometer to micron scale) and for a variety of different metals. *Template synthesis* involves the growth of carbon, metals, or polymers in the void volumes of a nonconductive porous host such as polycarbonate ultrafiltration membranes, porous Al<sub>2</sub>O<sub>3</sub> films, and track-etched mica crystals all of which possess long (microns or longer), dimensionally uniform pores. In general, these pores are oriented perpendicular to the plane of the porous film or membrane. Nanowires are produced by filling these pores with a conductive material. *Template synthesis*, however, is limited by its reliance on a template. Because all of the templates listed above possess linear, cylindrical (or prismatic) pores, only linear nanowires can be produced. Moreover, nanowires produced by *template synthesis* are limited to a maximum length that is equal to the thickness of the porous host membrane, which tends to range from 0.1 to 20 microns.

The *step edge decoration* method, which is described in publications by Himpsel<sup>3-4</sup>, Kern<sup>5-7</sup>, Behm<sup>2</sup> and others, involves the selective deposition of a metal or other material, such as CaF<sub>2</sub>, at atomic step edges on a vicinal single crystal surface.

*Step edge decoration* can be controlled to yield continuous "wires" of varied width and interwire spacing. Long nanowires that are many microns in length have been prepared. Because the dimension of the "wire" perpendicular to the vicinal surface has usually been limited to one or at most two atomic layers, it has not been possible to remove these ultra thin metallic ribbons from the surfaces on which they are synthesized. The technological utility of such nanowires is necessarily limited as a result.

In view of the foregoing, it would be desirable to provide methods that facilitate the fabrication of nanowires that are metallic, long (i.e., greater than ten microns in length), uniform in diameter, and removable from the surface on which they are synthesized and, thus, free standing.

#### SUMMARY OF INVENTION

The present invention is directed to methods that facilitate the fabrication of nanowires that are metallic, long (i.e., greater than ten microns in length), uniform in diameter, and removable from the surface on which they are synthesized and, thus, free standing. The fabrication processes of the present invention provide an electrochemical route to dimensionally uniform and mechanically robust metal nanowires that range in diameter from approximately 10-15 nm to approximately 1.0  $\mu\text{m}$ , and are up to approximately 1.0 mm or more in length. The metal nanowires produced by the methods of the present invention advantageously exhibit wire

diameter uniformity along the length of the wire as well as from wire-to-wire for thousands of nanowires. Preferably, the relative standard deviation from a mean diameter tends to be in a range of about 5 to 20 %, and more preferably is no more than about 10%. In addition, the metal nanowires produced by the methods of the present invention tend to be electrically continuous along their entire length, i.e., typically less than about 5% of the wires produced by the methods of the present invention tend to show any visible breaks.

The present invention includes three interrelated step-decoration methods that are based on the selective electrodeposition of a metal or metal oxide from an aqueous solution at step edges present on a basal plane-oriented surface, such as graphite, that is exposed to the solution. In a first innovative aspect of the present invention (Method I), metal oxide from an aqueous solution is selectively electrodeposited along step edges present on the stepped surface to form precursor metal oxide wires. The metal oxide nucleates at a high linear density along the step edges forming beaded chains of metal oxide nuclei, which, with continued deposition, rapidly grow into a hemicylindrical nanowires. Wire growth involves low overpotential deposition at constant, or nearly constant, deposition current. Once formed, the precursor metal oxide nanowires are preferably reduced in hydrogen gas ( $H_2$ ) at elevated temperatures to produce metal nanowires. Preferably this gas phase reduction occurs at about 500° C for about an hour.

In a second innovative aspect of the present invention (Method II), metal nanowires are prepared by direct electrodeposition of metal from an aqueous solution along step edges present on a stepped surface exposed to the solution. Following a nucleation pulse, the metal nucleates at a high linear density along the step edges forming beaded chains of metal nuclei, which, with continued deposition, grow into hemicylindrical nanowires. Wire growth involves low overpotential deposition at constant, or nearly constant, low deposition current. The deposition rates according to this method are preferably extremely low, e.g., the deposition rate to prepare a palladium nanowire via direct electrodeposition having a 200 nm diameter was about 10 minutes and a 300 nm diameter was about 20 minutes.

In a third innovative aspect of the present invention (Method III), beaded or hybrid metal nanowires comprising a first metal (metal A) into which nanoparticles of a second metal (metal B) have been inserted are prepared by first electrodepositing nanoparticles of metal B selectively along step edges of a step surface. The metal B nanoparticles are then capped with a molecular layer of an organic ligand having a strong affinity for the surface of the metal B nanoparticles. Metal A is then selectively electrodeposited along the step edges separating each metal B nanoparticle according to Method I or II. The ligand layer is preferably removed by heating the surface under reducing conditions in order to retain the metallic composition of the particles and connecting nanowire segments. The nanoparticles incorporated into the nanowires

may range in diameter from the diameter of the nanowire itself, e.g., as small as about 10 nm, to about 1.0  $\mu\text{m}$  or more.

In all three methods, the nanowires may be removed from the graphite surface by embedding the wires in a polymer film, and then peeling this film containing the  
5 embedded nanowires off of the graphite surface. This removal step makes the nanowires available for electrical characterization, for use as interconnects for connecting two nanometer-scale elements of a circuit, for the implementation of a variety of nanowire-based devices including sensors and biosensors, and for wiring of semiconductor quantum dots<sup>20</sup> to form a circuit. When used in sensors, the binding of  
10 an analyte molecule to the surface of the nanowire induces a measurable change in the nanowire conductivity.

Other objects and features of the present invention will become apparent from consideration of the following description taken in conjunction with the accompanying drawings.

## BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic diagram of Method I of the present invention for preparing metallic nanowires.

Figure 2 is a schematic diagram of a nanometer scale electric circuit incorporating an ensemble of metallic nanowires prepared in accordance with the  
20 methods of the present invention.

Figure 3 is a series of scanning electron microscope images of molybdenum nanowires prepared in accordance with Method I of the present invention.

Figure 4 is a typical cyclic voltammogram for  $\text{MoO}_4^{2-}$  at a highly oriented pyrolytic graphite electrode and scanning electron microscope images (above the cyclic voltammogram) of graphite surfaces obtained following the deposition of molybdenum dioxide ( $\text{MoO}_2$ ).

Figure 5 includes scanning electron microscope images of molybdenum nanowires embedded in a polystyrene film after removal from a graphite surface.

Figure 6 is a schematic diagram of Method II of the present invention for preparing metallic nanowires by direct electrodeposition of a metal.

Figure 7 includes cyclic voltammograms for a graphite electrode in two aqueous palladium plating solutions.

Figure 8 is a graph showing the diameters of palladium nanowires as a function of the deposition time for nanowires deposited using the plating solutions indicated in figure 7.

Figure 9 includes scanning electron micrographs of palladium nanowires prepared by electrodeposition from aqueous solutions indicated in figure 7.

Figure 10 includes scanning electron micrographs of 300 nanometer diameter palladium nanowires prepared in accordance with Method II of the present invention.

Figure 11 is a schematic diagram of Method III of the present invention for

preparing hybrid or beaded metal nanowires.

Figure 12 is a scanning electron micrograph image of a graphite surface following the implementation of the first three steps of Method III of the present invention.

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### DESCRIPTION

Referring in detail to the figures, methods that facilitate the fabrication of metallic nanowires and metallic nanowires prepared in accordance with the methods the present invention are shown. The methods of the present invention involve fabrication processes that provide an electrochemical route to dimensionally uniform, mechanically robust, long metal nanowires that are removable from the surface on which they are synthesized and, thus, free standing. The metal nanowires produced by the methods of the present invention tend to range in diameter from approximately 10-15 nm to approximately 1.0  $\mu\text{m}$  and tend to be greater than 10-20  $\mu\text{m}$  in length and preferably hundreds of microns in length on up to approximately 1.0 mm or more in length. The metal nanowires also advantageously exhibit high wire diameter uniformity along the length of the wire as well as from wire-to-wire for thousands of wires with a standard relative deviation from a mean diameter preferably in a range of about 5 to 20 % and more preferably no more than about 10%. In addition, the metal nanowires produced by the methods of the present invention tend to be electrically

continuous along their entire length, i.e., typically less than about 5% of the wires produced by the methods of the present invention tend to show any visible breaks.

The methods of the present invention include three interrelated step-decoration fabrication processes that are based on the electrodeposition of a metal or metal oxide from an aqueous solution on a basal plane-oriented surface, such as graphite, that is exposed to the solution. When suitable electric overpotentials are applied to the aqueous solution, the metal or metal oxide contained therein selectively deposits along the step edges present on the stepped surface forming "beaded-chains" of nuclei.

With continued deposition, the beaded chains form three-dimensional nanowires with diameters in a range of about 10-15 nm to 1.0  $\mu\text{m}$  for metal and in a range of about 20nm to 1.3  $\mu\text{m}$  for a metal oxide. The length of the nanowires tend to equal the length of the step edges on the stepped surface, which, with graphite in particular, tend to be equal to the grain diameter.

A first embodiment of the present invention, i.e., Method I, shown schematically in figure 1, includes a first step (Step 1) wherein precursor nanowires are selectively electrodeposited along the step edges present on a stepped surface from a dilute, preferably alkaline (pH of approximately 8.5), aqueous plating solution. The plating solution preferably includes an electrodepositable metal oxide at concentrations between about  $1 \times 10^{-3}\text{M}$  and about  $10 \times 10^{-3}\text{M}$  of the metal ion of interest. The metal oxide in the plating solution tends to nucleate at an extremely high

linear density, i.e., greater than approximately 20 nuclei/micron, along the step edges  
12 forming "beaded chains" of metal oxide nuclei. With continued deposition, these  
beaded chains rapidly become smooth, hemicylindrical precursor nanowires 14. As  
deposited, the precursor nanowires 14 tend to be brittle and nonconductive, but are  
5 highly uniform in diameter, with diameters in the range of about 20 nm to 1.3  $\mu\text{m}$ , and  
tend to be hundreds of microns to about 1.0 mm or more in length.

Method I of the present invention includes a second step (Step 2) which  
involves a gas phase reduction of the precursor metal oxide nanowires 14 at elevated  
temperatures. Preferably, the metal oxide nanowires 14 are reduced in hydrogen gas  
10 ( $\text{H}_2$ ) at about 500° C for about one hour to produce metallic nanowires 16 that retain  
the dimensional uniformity and hemicylindrical shape of the precursor, or "parent",  
metal oxide composite nanowires 14. The metallic nanowires 16 tend to be smaller in  
diameter (about 10-15 nm to 1  $\mu\text{m}$ ) than the parent nanowires 14 by about 30 to 35%,  
and tend to be mechanically resilient and electronically conductive.

15 In a third step (Step 3) of Method I, the gas phase reduced metal nanowires 16,  
which tend to be only weakly associated with the stepped surface 10, are embedded in  
a thin polystyrene film 18 that is cast onto the nanowires 16 and the graphite surface  
10. In a fourth step (Step 4) of Method I, the film 18, after it is allowed to air dry, is  
peeled off of the graphite surface 10 with the metal nanowires 16 embedded therein.  
20 The embedded nanowires 16 may comprise an ensemble of tens to hundreds of

nanowires or more. The ensemble of nanowires 20, which have been removed from the graphite surface 10 and, thus, are free standing, may advantageously be incorporated into an electronic circuit or sensor 22 as shown in figure 2. Low impedance electrical contacts 24 of silver, evaporated gold film and the like, may be connected to the ends of the nanowires 20.

Referring back to Figure 1, the system used for electrodeposition, i.e. Step 1, preferably includes a glass electrochemical cell having a volume of approximately 50 mL. The plating solution noted above is introduced into the cell along with three electrodes: A platinum "counter" electrode, a reference electrode (e.g., saturated calomel electrode), and a "working" electrode, which is the surface, such as graphite, on which the nanowires are to be grown. The two additional electrodes - i.e., the counter and reference electrodes - enable high precision control of the potential of the working electrode. All three electrodes are preferably connected to a three-electrode potentiostat (e.g., EG&G Model 273A) which may be programmed to apply the required potential to the working electrode.

The selective decoration of the step edges 12 and, thus, wire growth, in Step 1 occurs when the deposition is carried out at suitable overpotentials,  $\eta_{\text{dep}}$  (where  $\eta_{\text{dep}} = E_{\text{dep}} - E_{\text{eq}}$ ). Suitable overpotentials,  $\eta_{\text{dep}}$ , used in Step 1 for wire growth may range up to about (-)900mV versus the reversible potential<sup>1</sup>,  $E_{\text{eq}}$ , of the specific material involved. If the deposition is carried out using larger overpotentials, nucleation tends

to be spatially indiscriminant and metal oxide particles tend to be deposited everywhere on the surface of the step terrace 13. Moreover, if the overpotentials are too large, nucleation tends to occur on the surface of the step terrace 13 to the exclusion of the step edges 12.

The deposition process of Step 1 is preferably further characterized by the application of a constant, or nearly constant, deposition current over the deposition period, which is typically greater than 20 seconds to grow nanowires of a desired size. Preferably, the constant deposition current is in a range of about 10 to 200 microamps/cm<sup>2</sup> of electrode area. This rate invariance is consistent with a convection limited growth process where natural convective mixing of the electrolyte near an electrode surface occurs. Under these conditions the rate law for growth of a hemicylindrical solid becomes

$$r(t) = (2i_{\text{dep}} t_{\text{dep}} M / \pi n F \rho L)^{1/2} \quad (1)$$

where  $r(t)$  is the radius of the hemicylindrical nanowire,  $i_{\text{dep}}$  is the deposition current,  $t_{\text{dep}}$  is the deposition time,  $M$  is the atomic weight of the deposited metal,  $n$  is the number of electrons transferred per metal atom,  $F$  is the Faraday constant, i.e., 96,485 C eq<sup>-1</sup>,  $\rho$  is its density, and  $L$  is the total length of the nanowire(s) on the electrode surface. As indicated by Equation 1, the nanowire diameter is directly proportional to the square root of the deposition time. As a result, nanowires of a particular diameter can be selectively produced by the methods of the present

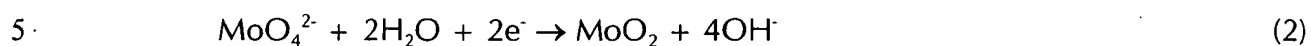
invention. Further, because  $dr/dt$  is proportional to  $t^{-1/2}$ , the growth of highly dimensional uniform structures, i.e., populations of nanowires that are narrowly dispersed with respect to wire diameter, is possible.

As indicated above, the diameter of the precursor nanowires 14 range from about 20 nm to 1.3  $\mu\text{m}$ , which is typically many times the height of the step edge 12 responsible for nucleating the growth of the wire 14. The height of the step edge 12 is typically about 0.3 to 2.0 nm. Two factors tend to contribute to this "amplification" of the step edge 12. First, at the low deposition potentials used in the methods of the present invention, the incipient nucleation sites tend to be confined to the step edges 12 on the graphite surface 10, which helps prevent the "spread" of the nanowire 14 onto terraces 13 during growth. The second factor is the inherent hemicylindrical symmetry of diffusional transport to metal nuclei arrayed along a linear step. The nanowire 14 ends up with a hemicylindrical cross-section because the ionic transport to the surface of the growing wire has this symmetry. These two factors operate in concert and permit the growth of hemicylindrical wires with virtually any diameter from step edges having molecular dimensions.

It should be understood that Method I may be used to produce metal nanowires from any conductive metal oxide that is electrodepositable, including  $\text{MoO}_2$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , and the like. The fabrication of molybdenum nanowires is described below with regard to figures 3-5 for exemplary purposes only. See also Zach et al., *Science*

290 (2000) 2120<sup>28</sup>, which is incorporated by reference as if set forth in full.

To prepare molybdenum nanowires in accordance with Method 1 shown in figure 1, molybdenum dioxide (MoO<sub>2</sub>) is first electrodeposited (Step 1) according to the reaction:



Under the conditions employed in Step 1, i.e., low overpotentials in a range of about -600 mV to -800mV and constant, or nearly constant, deposition current in a range of about 10 to 200 microamps/cm<sup>2</sup>, MoO<sub>2</sub> nucleates at an extremely high linear density (greater than about 20 nuclei/μm) along the step edges 12. The deposited MoO<sub>2</sub> forms "beaded chains" of 5-8 nm diameter MoO<sub>2</sub> nuclei which, with continued deposition, rapidly become smooth, hemicylindrical nanowires. Figure 3 shows a series of MoO<sub>2</sub> nanowires electrodeposited according to Step I of Method 1 along step edges of a stepped graphite surface. As shown in figure 3, the MoO<sub>2</sub> nanowires include nanowires with diameters of 13 nm, 62 nm, 130 nm and 210nm. The numbers at the upper left indicate the deposition time, in seconds, i.e., 1s, 4s, 16s, and 256s, for preparing these MoO<sub>2</sub> nanowires from an aqueous solution containing 1.0 mM MoO<sub>4</sub><sup>2-</sup> by applying a deposition potential of about -0.75 V vs. SCE.

A typical cyclic voltammogram for MoO<sub>4</sub><sup>2-</sup> at a highly oriented pyrolytic graphite electrode is shown in figure 4. As figure 4 indicates, the selectivity of MoO<sub>2</sub> nucleation is controlled by the deposition potential. The scanning electron

microscopy (SEM) images (above the cyclic voltammogram) of the graphite surfaces were obtained following deposition at potentials in a range of about (-)0.7 to (-)0.9 V versus a saturated calomel electrode (SCE) (right) and in a range of about (-)1.25 to (-)1.4 V versus SCE (left). As shown, electrodeposition of  $\text{MoO}_x$ , which has a reversible potential of about 0.1V, occurred with a high degree of selectivity at step edges at deposition overpotentials in the range of (-)0.6 to (-)0.8 V versus SCE (right). The application of a deposition potential more negative than (-) 1.0 V (left) caused particle growth at surface terraces.

Once formed,  $\text{MoO}_x$  nanowires may be reduced in  $\text{H}_2$  at  $500^\circ\text{C}$  to produce metallic molybdenum ( $\text{Mo}^0$ ) nanowires (Step 2). These metal nanowires are smaller in diameter by about 30% to 35% as compared with the parent  $\text{MoO}_x$  wires, and are only weakly associated with the graphite surface. Removal of these reduced wires from the graphite surface is accomplished by embedding the nanowires in a polystyrene film (Step 3), and lifting this film together with the embedded nanowires off the graphite surface (Step 4). Figure 5 provides SEM images of molybdenum nanowires embedded in a polystyrene film after removal from a graphite surface. The ability to remove molybdenum nanowires from the graphite surfaces on which they are synthesized facilitates the technological utility of these nanostructures both in electronic devices, as interconnects, and in sensors.

Turning to figure 6, a second embodiment of the present invention, Method II,

is shown schematically to involve the preparation of metal nanowires by "direct" electrodeposition of a metal on a stepped surface 110, such as graphite, that is exposed to an aqueous solution containing the metal. In a first step (Step 1), nanowires 116 are selectively electrodeposited along the step edges 112 present on a stepped surface 110 from an aqueous plating solution comprising a electrodepositable metal. The solution preferably includes metals such as palladium, gold and the like, at concentrations between about  $1 \times 10^{-3}$  and  $10 \times 10^{-3} \text{M}$  of the metal ion of interest. Electrodeposition of gold, however, is preferable performed in an electrochemical cell that is pressurized to about 40 atm. Following a nucleation pulse, the metal in the plating solution nucleates at an extremely high linear density (i.e., greater than about  $20/\mu\text{m}$ ) along the step edges 112 forming "beaded chains" of metal nuclei, which, with continued deposition, become smooth, hemicylindrical nanowires 116.

Preferably, the electrodeposition is carried out at very low deposition overpotentials of up to about (-)400mV and preferably in a range of about (-)10 to (-)200mV. To increase nucleation density and , thus, ensure that the nanowires are continuous, a nucleation pulse, well negative of the reversible potential, may be applied for about five milliseconds prior to electrodeposition at the desired overpotential. The deposition is preferably carried out at low constant, or nearly constant, deposition current, e.g., preferably less than  $50 \text{mA}/\text{cm}^2$ . Depending on the metal being deposited and the applied current density, which is preferably in a range

of about  $5\mu\text{Acm}^{-2}$  to  $50\mu\text{Acm}^{-2}$ , the deposition rates in Method II are preferably extremely low. For example, as shown in figure 8 and discussed below, the deposition time to prepare a palladium nanowire having a 200 nm diameter was about ten minutes. Deposition rates to prepare metal nanowires of a desired diameter may be determined according to Method II may be calculated using Equation (1).

In a second step (Step 2) of Method II, the metal nanowires 116 are embedded in a thin polystyrene film 118 that is cast onto the nanowires 116 and the graphite surface 110. In a third step (Step 3), the film 118, after it is allowed to air dry, is peeled off of the graphite surface 110 with the metal nanowires 116 embedded therein. The embedded nanowires 16 may comprise an ensemble of tens to hundreds of nanowires or more. The ensemble of nanowires, which have been removed from the graphite surface 110, may also advantageously be incorporated into an electronic circuit or sensor 22 as shown in figure 2.

Palladium nanowires prepared in accordance with Method II are described in regard to figures 6-10 for exemplary purposes only. Palladium nanowires may be electrodeposited from aqueous solutions containing palladium. Examples of such solutions include 2.0 mM  $\text{Pd}^{2+}$ , 0.1 M HCl, water, and 2.0 mM  $\text{Pd}^{2+}$ , 0.1 M  $\text{HClO}_4$ , and the like. Palladium nanowires prepared by the process of Method II are shown in figures 9-10. Starting with a freshly cleaved graphite surface within a palladium plating solution, these nanowires were prepared by first applying a 5 ms nucleation

pulse of  $-0.2$  V (vs. saturated calomel electrode, SCE). As shown in figure 7, this potential is well negative of the reversible potential for palladium deposition in these solutions ( $+0.6$  to  $+0.7$  V vs. SCE). After this nucleation pulse, the growth of palladium nanowires was carried out using potentials in the ranges shown in gray in figure 7. These deposition potentials produce deposition current densities ranging from about  $30\text{--}60\ \mu\text{A cm}^{-2}$  and deposition times for  $200\text{ nm}$  diameter wires of about 10 minutes (see figure 8). The deposition times for palladium nanowires having  $300\text{ nm}$  diameters, as shown in figure 10, were about 20 minutes.

The morphology of the palladium nanowires, as well as other metal nanowires, obtained by electrodeposition tends to be dependent on the identity of the electrolyte present in the plating solution. For example, palladium nanowires deposited from HCl solutions, as shown in figure 9 (left), tend to be rough and granular. The dimensions of the grains in these polycrystalline wires as estimated from SEM images ranged from about  $50$  to  $300\text{ nm}$ . Continuous nanowires of  $150\text{ nm}$  in diameter have been obtained from this solution. Deposition of palladium nanowires from  $\text{HClO}_4$  solutions as shown in figure 9 (right), yield nanowires having a smoother morphology. The grains in these nanowires were  $10\text{--}50\text{ nm}$  in diameter. A smoother morphology permits nanowires as narrow as  $55\text{ nm}$  in diameter to be deposited. The rough and smooth nanowires prepared using these two plating solutions behave electrically identical to one another.

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A third embodiment of the present invention, Method III, involves the preparation of beaded or hybrid metal nanowires comprising a first metal (metal A) into which nanoparticles of a second metal (metal B) have been inserted. These hybrid metal nanowires are prepared, as shown schematically in figure 11, by first (Step 1) electrodepositing nanoparticles 215 of metal B selectively along step edges 212 of a stepped surface 210 such as graphite. The metal B nanoparticles 215, which are preferably formed from a noble metal including nickel, palladium, platinum, gold, and the like, are electrodeposited, e.g., from an aqueous solution comprising  $1.0 \times 10^{-3} \text{M}$  to  $10 \times 10^{-3} \text{M}$  of the metal ion of interest using a suitable overpotential. Platinum nanoparticles, for example, are preferably deposited for 100ms from a  $1.0 \times 10^{-3} \text{M}$   $\text{Pt}^{2+}$  solution using an overpotential of  $-0.5 \text{V}$  in order to obtain 10nm diameter metal nanoparticles at a density of about  $10^8$  to  $10^{10} \text{ cm}^{-2}$ . See, e.g., Zach et al., *Adv. Mat.*, **12** (2000) 878<sup>29</sup> and Zoval et al., *J. Phys. Chem. B.* **102** (1998) 1166<sup>30</sup>, and others which are incorporated by reference as if set forth in full.

The deposited metal B nanoparticles 215 are then (Step 2) exposed to an ethanolic solution of an alkane thiol. As a result of the thiol exposure, each nanoparticle is "capped" by a self assembled molecular monolayer of an organic ligand 217 having a strong affinity for the surface of the metal B nanoparticles 215. Examples of such ligands include Thiols (chemical formula:  $\text{R-SH}$  where R is a hydrocarbon), which have an affinity for noble and coinage metals including Pt, Pd,

Au, Ag, and Cu, and Nitriles (chemical formula: R-CN where R is a hydrocarbon), which have an affinity for Pt, Pd and Ag.

In a next step (Step 3), a metal A or a metal A oxide is selectively electrodeposited along the step edges 212 separating each metal B nanoparticle 215 according to Method I or II discussed above to form a metal A or metal A oxide nanowire 214, 216 between the metal B nanoparticles 215. Because the ligand 217 forms an electrically insulating layer atop of the metal nanoparticles 215, the deposition of the wire material does not occur on top of the nanoparticles 215, just between the nanoparticles 215.

In a final step (Step 4), the ligand layer 227 is preferably removed by heating the surface under reducing conditions in order to retain the metallic composition of the particles 215 and connecting nanowire segments 216. Preferably, the reduction of the surface occurs in H<sub>2</sub> at 500° C, which results in the alkane thiol being pyrolysed. The nanoparticles incorporated into the nanowires may range in diameter from the diameter of the nanowire itself, e.g., as small as about 10 nm, to about 1.0 µm or more. Figure 12, which is a SEM image of a graphite surface following Step 3 of Method III, shows hybrid nanowires comprising nickel nanoparticles and molybdenum dioxide nanowire segments prepared according to Method III.

Like the metal nanowires prepared according to Methods I and II (see figures 1 and 6), the hybrid nanowires prepared according to Method III may be removed from

the graphite surface by embedding the wires in a polymer film, and then peeling this film containing the embedded nanowires off of the graphite surface. Because the hybrid nanowires are removable they may be utilized as elements of nanometer-scale circuits, sensors, biosensors, and the like. When used in sensors, the nanowire segments are employed to "read-out" any measurable change in the nanoparticle conductivity induced by the binding of an analyte molecule to the surface of the nanoparticle.

While the invention is susceptible to various modifications and alternative forms, specific examples thereof have been shown in the drawings and are herein described in detail. Many alterations and modifications can be made by those having ordinary skill in the art without departing from the inventive concepts contained herein. It should be understood, therefore, that the illustrated embodiments have been set forth only for the purposes of example and that they should not be taken as limiting the invention.

#### CITED REFERENCES

1. Bard, A.J., et al., "Electrochemical Methods, Fundamentals and Applications," 2<sup>nd</sup> Ed., Wiley, New York, 2001 (ISBN0-471-04372-9)
2. Behm, R.J. et al., Phys. Rev. Lett. 1999, 11, 447-449, 427.
3. Himpsel, F. J. et al., Surface Review and Letters 1997, 4, 371-380.
4. Himpsel, F. J. et al., J. Mrs Bulletin 1999, 24, 20-24.
5. Kern, K. et al., Kern, K. Surf. Sci. 1998, 414, L964-L969.
6. Kern, K. et al., Phys. Rev. B 2000, 61, 2254-2262.
7. Kern, K. et al., Phys. Rev. B 2000, 61, R5133-R5136.
8. Martin, C. R. et al., Chem. Mat. 1999, 11, 1183-1185, 1185A.
9. Martin, C. R. Adv. Mat. 1991, 3, 457-459.
10. Martin, C. R. et al., Nanostructured Materials 1997, 9, 705-708.
11. Martin, C. R. et al., J. Phys. Chem. 1994, 98, 2963.
12. Martin, C. R. et al., J. Phys. Chem. 1992, 96, 9001-9007.
13. Martin, C. R. et al., J. Phys. Chem. 1992, 96, 9001.

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14. Martin, C. R. et al., *J. Mat. Res.* 1994, 9, 1174-1183.
15. Martin, C. R. et al., *J. Am. Chem. Soc.* 1991, 113, 3174-3175.
16. Moskovits, M. et al., *M. J. Phys. Chem.* 1993, 97, 8495-8503.
17. Moskovits, M. et al., *J. Phys. Chem.* 1996, 100, 14037-14047.
18. Moskovits, M. et al., *Phys. Rev. B* 1998, 57, 13550-13553.
19. Myrick, M. L. et al., *J. Electrochem. Soc.* 1998, 145, 3320-3328.
20. Penner, R.M. et al., *Acc. Chem. Res.*, 33 (2000) 78.
21. Searson, P.C. et al., *App. Phys. Lett.* 73 (1998) 1436-1438.
22. Searson, P.C. et al., *Phys. Rev. B* 61(2000) R6463-R6466
23. Searson, P.C. et al., *Journal of Electronic Materials* 24 (1995) 955-960.
24. Searson, P.C. et al., *Science* 261 (1993) 1316-1319.
25. Searson, P.C. et al., *Phys. Rev. B* 51 (1995) 7381-7384.
26. Searson, P.C. et al., *Phys. Rev. B* 58 (1998) R14681-R14684
27. Searson, P.C. et al., *App. Phys. Lett.* 74 (1999) 2803-2805.
28. Zach et al., *Science* 290 (2000) 2120.
29. Zach et al., *Adv. Mat.*, 12 (2000) 878.
30. Zoval et al., *J. Phys. Che. B.* 102 (1998) 1166.